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<b>(21) International Application Number:</b> PCT/US96/20219 <b>(22) International Filing Date:</b> 19 December 1996 (19.12.96)  <b>(30) Priority Data:</b> 9600030.2      3 January 1996 (03.01.96)      GB  <b>(71) Applicant (for all designated States except US):</b> S.C. JOHNSON & SON, INC. [US/US]; 1525 Howe Street, Racine, WI 53403 (US).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> ADAT, Balvinder [GB/GB]; 81 Pevensey Way, Paddock Hill, Frimley Green, Camberley, Surrey GU16 5UU (GB).  <b>(74) Agents:</b> BOZEK, Laura, L. et al.; S.C. Johnson & Son, Inc., Patent Section, 1525 Howe Street, Racine, WI 53403 (US).		<b>(81) Designated States:</b> AU, BR, CA, CN, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CLEANING COMPOSITIONS  <b>(57) Abstract</b>  An aqueous liquid storage stable foamable limescale removing composition comprising a mixture of sulphamic acid and at least one organic carboxylic acid, a thickening agent and an amine oxide surfactant.		

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## CLEANING COMPOSITIONS

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### Technical Field

This invention relates to cleaning compositions particularly for use in removing limescale stains from surfaces, particularly compositions that are dispensable as foams.

### Background Art

10 Tap water always contains a certain amount of solubilized ions which eventually deposit as salts, on surfaces in contact with the water, as it evaporates. Such salts include calcium carbonate, commonly referred to as limescale. This phenomenon of limescale accumulation on surfaces which are often in contact with water may damage surfaces and affects the functioning of taps or appliances, such as irons. Also, the accumulation of  
15 limescale in the toilet bowl is aesthetically unpleasant and favors the deposition of further soil and the growth of microorganisms. It is therefore important to control this limescale accumulation.

Many limescale removing compositions are known in the art. For example, EP-A-0,589,761 discloses a thickened acidic aqueous cleaner for bathtubs and other hard  
20 surfaced items, which removes limescale, soap scum and greasy soil from surfaces of such items without damaging such surfaces.

One composition of the reference comprises:

- (a) an anionic surfactant;
- (b) a nonionic surfactant;
- 25 (c) a xanthan gum thickener having a molecular weight of about 1,000,000 to 10,000,000 such as Kelzan® T sold by Merck & Co.; and
- (d) 2 to 8 percent of an acid mixture of succinic acid; glutaric acid and adipic acid of about 1:1:1; and
- (e) balance being water, wherein the composition has a pH of about 1 to  
30 about 4, more preferably about 2.7 to about 3.3 and a Brookfield viscosity of about 200

to 1,000 cps at room temperature. using a #2 spindle and 50 rpm. The composition of the reference does not include either sulfamic acid or amine oxide surfactants.

EP-A-0,606,712 discloses a thickened buffered aqueous acidic composition.

5 The composition of the reference comprises citric acid and sodium citrate, and in the composition suitable thickeners include conventional thickeners such as xanthan gum, polymers, alkyl amines, and surfactant based thickeners as well as nonionic and amine oxide surfactants. The composition of the reference does not include sulphamic acid.

10 EP-A-0,666,304 discloses compositions comprising as a first essential ingredient an organic acid such as maleic acid. It is preferred in the invention of the reference to use maleic acid either alone or together with sulfonic acids such as sulfamic acid.

The compositions according to the reference invention comprise as a second essential ingredient a surfactant or mixtures thereof. The compositions comprise said surfactant in an appropriate amount below 1% by weight of the total composition. The  
15 composition of the reference does not include amine oxide surfactants. Optionally, the compositions of the reference comprise thickeners.

WO-A-94 28108 concerns oven cleaning compositions and does not deal with acidic limescale removing compositions.

20 The subject invention is directed to a limescale removing composition which can be delivered as a foam.

In one embodiment, the subject invention provides an aqueous liquid storage-stable limescale removing foamable composition comprising:

- a. a mixture of sulphamic acid and at least one organic carboxylic acid;
- b. a thickening agent;
- 25 c. an amine oxide surfactant.

In another embodiment, the subject invention provides a method of removing limescale from a substrate using the composition as set out above.

### **Disclosure of Invention**

All amounts of components set out herein are given as percentages by weight of the limescale removing composition.

5        The composition of the invention comprises a mixture of sulphamic acid and at least one organic carboxylic acid. The sulphamic acid and the at least one other acid are preferably mixed in synergistically effective limescale removing amounts. Preferably, the organic carboxylic acid has a molecular weight of 60-250. More preferably, the carboxylic acid is lactic acid, citric acid, or another hydroxy acid where the hydroxy  
10       group is  $\alpha$  to at least one of the acid moieties.

Preferably, the mixture of acids is present in the range 5-20 weight percent of the aqueous cleaning composition and more preferably 10-20 weight percent.

The composition of the invention can be dispensed as a foam through a foam dispenser. The composition may tend to be difficult to dispense in this way if the  
15       composition in use has a final viscosity which is much above 300 cps. All viscosity measurements stated herein are taken using a Brookfield viscometer, at 20°C using #3 spindle at 30 rpm. Preferably, the final viscosity is in the range 200-300 cps. When the maximum viscosity of the composition of the invention is limited by the need for the composition to be dispensable through a foam dispenser, one aspect of particular  
20       importance is storage stability. The composition of the subject invention relies on a complex blend of components and inevitably the composition will be placed into its final package some long time before it comes into use in the hands of the ultimate consumer. It is important that the viscosity of the composition is maintained within parameters during storage to allow delivery through the foam dispenser. Long term stability of the  
25       viscosity is mainly determined by the optimized level and type of thickening agents. Thickeners which can be effective in the composition of the subject invention can be selected from the group consisting of acrylic emulsion polymer thickeners, xanthan gums, rhamsan gums, welan gums and polyurethanes. The preferred thickener is xanthan gum with altered rheology. Preferably, the thickener is present in an amount of 0.001-5  
30       weight percent based on the weight of the cleaning composition.

The storage stable composition of the subject invention will preferably be dispensable as a foam through a foam dispenser after storage at room temperature for 6 months, and more preferable after storage at room temperature for 1 year. Preferably, the storage stable composition of the subject invention will not show phase separation or precipitation after said storage, the viscosity of the composition remaining constant during said storage.

Typically, the foaminess index  $\Sigma$  is between 15-50 and more typically between 20-30.

While the amount of thickener is instrumental in allowing the composition to remain storage stable, it should also be noted that the presence of particular amounts of other components in the composition may effect viscosity. In particular, the amine oxide surfactant can be expected to have an effect on the viscosity of the composition.

Another important feature of the limescale removing composition of the invention is that the composition is dispensable as a foam.

Dispensing as a foam allows the composition to remain on the limescale stain for an effective time. The composition should be able to remain in contact with and be able to wet and penetrate the limescale stain for a sufficient time to have an effective descaling effect. Subsequently, the composition must be able to be washed away easily with water.

Of importance, therefore, in the effectiveness of the composition is the quality of the foam which is produced. At one extreme, foams can be loose airy type foams, while at the other extreme, foams can be tight mousse like type foams. The composition of the subject invention ideally produces a foam which is roughly halfway between a loose airy type foam and a tight mousse type foam in order to give maximum descaling and a good cling parameter. Cling is measured by spraying about 10g of product onto the underside of a preweighed suspended plate weighing about 200g. The plate is left to hang for 5 minutes and is then re-weighed. The cling is determined by the amount of product remaining on the plate after 5 minutes. Preferably, the cling parameter of the composition of the subject invention is 50 - 70% of product remaining on the surface after 5 minutes.

The nature and amount of the amine oxide surfactant present in the composition of the invention will generally determine the foam profile and cling parameter of the composition. Additionally, however, the cling parameter is dependent on the amount of thickener present in the composition. The amine oxide preferably has the formula  $RR'R''NO$ , where R is a substituted or unsubstituted alkyl or alkene group containing from about 8 to about 30, preferably from about 10 to about 20, more preferably about 10 to 16 carbon atoms. Preferably, R is an unsubstituted alkyl group. Groups R' and R'' are each substituted or unsubstituted alkyl or alkene groups containing from about 1 to about 18, preferably from about 1 to about 4, carbon atoms. More preferably, R' and R'' are each methyl groups.

The amine oxide detergent surfactant can be prepared by known and conventional methods. One such method involves the oxidation of tertiary amines in the manner set forth in U.S. Patent No. 3,223,647 and British Patent 437,566. In general terms, amine oxides are prepared by the controlled oxidation of the corresponding tertiary amines.

Most preferably, the surfactant will be lauryl dimethyl amine oxide. Preferably, the amine oxide surfactant is present in the amount of 2.0-8.0% by weight of the total composition.

The composition can contain other optional components appropriate to limescale removing compositions including dyes and fragrances.

The balance of the composition of the invention (to 100 weight percent) is deionized water.

The composition of the invention is dispensable through a conventional foam dispenser.

**Modes for Carrying Out the Invention**

Exemplary compositions of the invention are now set out below:

**Example 1**

5	<b><u>Material</u></b>	<b><u>% w/w</u></b>
	Deionized Water	To balance
	Xanthan gum with altered rheology (Kelco)	0.50
	Sulphamic Acid (GelpKe and Bate Ltd.)	10.00
	Citric Acid	4.00
10	Lauryl dimethyl amine oxide	2.00
	1% Dye Solution - Blue	0.50
	Fragrance	0.10



Example 2

<u>Material</u>	<u>% w/w</u>
Deionized Water	To balance
Xanthan gum with altered rheology (Kelco)	0.70
5 Sulphamic Acid (GelpKe and Bate Ltd.)	9.00
Lactic Acid (Purac®)	5.00
Lauryl dimethyl amine oxide	4.00
1% Dye Solution - Blue	0.30
Fragrance	0.20

**Example 3**

<b><u>Material</u></b>	<b><u>% w/w</u></b>
Deionized Water	To balance
Xanthan gum with altered rheology (Kelco)	0.60
5 Sulphamic Acid (GelpKe and Bate Ltd.)	13.00
Lactic Acid (Purac®)	1.00
Lauryl dimethyl amine oxide	5.00
1% Dye Solution Acid Blue 7	0.40
Fragrance	0.10

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The composition of Example 3 had a viscosity of 250 cps and on dispensing through a conventional foam dispenser produced a foam with a cling parameter of 50 - 70% over a 5 minute period.

The composition was stable on storage at room temperature for one year.

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The composition of Example 3 was tested for effectiveness by the marble cube test as follows:

**Marble Cube Test**

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1) 3 marble cubes weighing approximately 20g were washed with distilled water and dried in an oven until their weight was constant at room temperature.

2) Each marble cube was weighed ( $W_0$ ).

3) 150g of product being tested was weighed into a conical flask.

4) The pre-weighed marble cubes were placed into the test product.

25

5) The marble cubes were left on test for 18 hours.

6) After 18 hours, the marble cubes were removed from the test product and rinsed thoroughly with deionized water.

7) Each marble cube was dried in an oven for 12 hours and weighed at room temperature. ( $W_1$ )

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The percentage descaling was calculated as follows:

$$W_0 - W_1 \times 100\% = \% \text{ weight loss.}$$

### **Interpretation of Results**

5 The higher the percentage weight loss the greater the limescale removal activity of the product.

### **Results of the above Marble Cube Test**

10 For the composition of Example 3, the average % weight loss (for the 3 cubes) ranged from 35 - 40%.

### **Comparative Example 1**

A commercially available maleic acid limescale removing composition was tested in the same way as above and the % weight loss ranged from 20 - 30%.

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### **Industrial Applicability**

The subject invention provides a limescale removing composition which may be produced using conventional manufacturing methods and packaging. The foamable limescale removing composition maintains its foaming and rheological properties after shelf storage at room temperature for 6 months, preferably one year. This shelf stability will allow a consumer to effectively utilize the descaling composition even though the composition may be placed into its final package a long time prior to its purchase and use.

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**CLAIMS:**

1. An aqueous liquid storage stable foamable limescale removing composition comprising:
  - 5 a. a mixture of sulphamic acid and at least one organic carboxylic acid;
  - b. a thickening agent;
  - c. an amine oxide surfactant.
- 10 2. The composition according to claim 1 wherein the viscosity of the composition is 300 cps or less.
3. The composition according to claim 1 wherein the viscosity of the composition is in the range of 200 cps to 300 cps.
- 15 4. The composition according to claim 1 wherein the composition has a cling parameter of 50 - 70%.
5. The composition according to claim 1 wherein at least one carboxylic acid is lactic acid.
- 20 6. The composition according to claim 1 wherein at least one carboxylic acid is citric acid.
7. The composition according to claim 1 wherein the thickening agent is selected from the group consisting of acrylic emulsion polymers, xanthan gums, rhamosan gums, welan gums and polyurethane.
- 25 8. The composition according to claim 1 wherein the amine oxide surfactant is an alkyl amine oxide surfactant.

9. The composition according to claim 8 wherein the alkyl amine oxide surfactant is a C<sub>10</sub>-C<sub>16</sub> alkyl dimethyl amine oxide.
10. The composition according to claim 9 wherein the alkyl amine oxide surfactant is lauryl dimethyl amine oxide.
11. The composition according to claim 1 wherein said mixture of sulphamic acid and at least one organic carboxylic acid are admixed together in synergistically effective limescale removing amounts.
12. An aqueous liquid storage stable foamable limescale removing composition comprising:
- 5-20% by weight of a mixture of sulphamic acid and at least one organic carboxylic acid;
  - 0.001-5% by weight of a thickening agent;
  - 2.0-8.0% by weight of an amine oxide surfactant wherein the balance of the composition is deionized water.
13. A method of removing limescale from a substrate comprising the steps of applying the composition of claim 1 to a substrate containing limescale; allowing the composition to remain in contact with the substrate for a sufficient amount of time to have a descaling effect; and removing the composition from the substrate.
14. The method of removing limescale from a substrate according to claim 13 wherein the composition comprises: 5-20% by weight of a mixture of sulphamic acid and at least one organic carboxylic acid; 0.001-5% by weight of a thickening agent; 2.0-8.0% by weight of an amine oxide surfactant wherein the balance of the composition is deionized water.

# INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D3/34 C11D17/00 C11D1/75

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 130 786 A (ECONOMICS LAB) 9 January 1985 see the whole document ---	1-4,6-14
X	GB 1 240 469 A (ATLAS PRESERVATIVE CO LTD) 28 July 1971 see claims ---	1,2, 8-11,13
Y	FR 2 469 450 A (SOLITAIRE PRODUITS ENTRETIEN F) 22 May 1981 see the whole document ---	1-14
Y	EP 0 253 676 A (R & C PRODUCTS PTY LTD) 20 January 1988 see claims ---	1-14
	-/-	

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A	<p>EP 0 656 417 A (PROCTER &amp; GAMBLE) 7 June 1995  see the whole document  -----</p>	1-14

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat. Application No

PCT/US 96/20219

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0130786 A	09-01-85	US 4587030 A AU 558507 B AU 2999584 A CA 1224998 A JP 1723311 C JP 4007400 B JP 60051800 A	06-05-86 29-01-87 10-01-85 04-08-87 24-12-92 10-02-92 23-03-85
GB 1240469 A	28-07-71	NONE	
FR 2469450 A	22-05-81	BE 886064 A DE 3042507 A	07-05-81 21-05-81
EP 0253676 A	20-01-88	AU 602707 B AU 7578787 A DK 170538 B EG 18545 A ES 2022360 T IE 60070 B IN 172271 A JP 63024000 A KR 9506289 B NO 175967 B	25-10-90 21-01-88 16-10-95 30-07-93 01-12-91 01-06-94 29-05-93 01-02-88 13-06-95 03-10-94
EP 0656417 A	07-06-95	AU 1214195 A CA 2173438 A WO 9514641 A	13-06-95 01-06-95 01-06-95



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